

DEACTIVATION AND ACTIVATION OF IMPURITIES IN SILICON

K. D. Glinchuk and N. M. Litovchenko

Translation of "Dezaktivatsiia i aktivatsiia domishok v kremnii"

Ukrainskii Fizichnii Zhurnal, Vol. 10, No. 2, pp. 172-177, 1965

FACILITY FORM 602

N66-21686	
(ACCESSION NUMBER)	(THRU)
14	1
(PAGES)	(CODE)
	26
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 1.00Microfiche (MF) .50

ff 653 July 65

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON
FEBRUARY 1966

DEACTIVATION AND ACTIVATION OF IMPURITIES IN SILICON

K. D. Glinchuk and N. M. Litovchenko

ABSTRACT

21686

/172*

Investigation of the effect of annealing in the range from 800 to 1200°C on the electrical behavior of impurity atoms of Au, Zn, Pt, S, and Fe in silicon semiconductors. Annealing at 800°C is found to make such impurities inactive, suppressing their effects on silicon photoconductivity and electron and hole concentrations. The effects are restored by annealing at 1200°C. Changes in solubility of these impurities in silicon and shifts in their diffusion direction at different temperatures are seen to be major factors in the mechanism of the phenomenon.

autha

Impurities in semiconductors may be found in active and passive states (ref. 1). When in an active state, they create a spectrum of energy levels in the forbidden zone which affects the concentration of equilibrium electrons (n_0 and p_0) and the lifetime of nonequilibrium electrons (τ_e) and holes (τ_d). In an inactive state, these impurities do not create any energy levels, that is they do not affect the electrophysical properties of semiconductors.

The investigation described in this article involved a study of the change of Au, Zn, Pt, Fe and S impurities in silicon from an active to an inactive state, and vice versa.

*Numbers given in the margin indicate the pagination in the original foreign text.

The Investigation Methods

A study was made of impurities whose concentration $N \approx 10^{16}-10^{17} \text{ cm}^{-3}$ was introduced by the diffusion method at a temperature of $1200-1250^\circ\text{C}$ ($D_{1200^\circ\text{C}} \approx 10^{-6}-10^{-8} \text{ cm}^2/\text{sec}$ (refs. 2 and 3) into n- and p-type single-crystal silicon samples whose conductivity was determined by a slightly ionized donor ($N_d = n_0$) or acceptor ($N_a = p_0$) impurity. The impurities were diffused in unsoldered quartz ampoules from a vapor phase (S, Zn), from an electrolytically coated metal film (Zn, Fe) or a pulverization in a vacuum (Au, Pt).¹ After the diffusion the samples were case-hardened by dropping the ampoules into oil.

To change the state of the impurities under investigation, the samples were annealed at different temperatures.²

The change in the concentration and state of the impurity can be judged by watching the change in the concentration and lifetime of the current carriers, inasmuch as the investigated Au, Zn, Pt, Fe and S impurities create a spectrum of donor and acceptor levels $E_{1,2}$ in the forbidden zone of the silicon (fig. 1) which have a considerable effect on these parameters (refs. 2, 3 and 6).

The surfaces of the samples were polished and etched at 0°C in a mixture consisting of 1 part HF + 1 part CH_3COOH + 2 parts 98 percent HNO_3 . In this case, a 500 mμ layer had to be removed from the surface of the sample inasmuch as it was found to have a higher conductivity than the rest of the

¹The time required for the complete deactivation of a sample by an impurity can be determined by the following formula $t \approx 4d^2/\pi^2D$, where d is the thickness of the sample (ref. 4).

²The change in the concentration and lifetime of the current carriers in the heat-treated control samples is similar to the one described in reference 5.

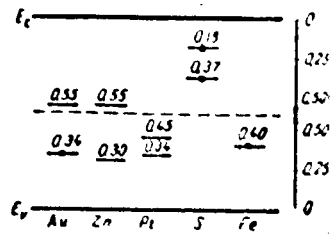


Figure 1. Donor (●) and acceptor (-) levels produced by impurity atoms of Au (ref. 2), Zn (ref. 2), Pt (ref. 6), S (ref. 3) and Fe (ref. 2) in silicon.

Energy level spectrum corresponds to various charged states of impurity atoms.

sample after the heat treatment (see below). The contacts were made from Au + 1 percent Sb and Zn + 20 percent Ga alloys for n- and p-type silicon, respectively.

Discussion of the Results

1. Deactivation of impurities. Shown in figure 2 (curves 2 and 3) are the typical data illustrating the change in the concentration of the current carriers and their temperature dependence as the Au, Zn, Pt, Fe and S impurities change from an active to an inactive state. The concentration of current carriers in the initial samples (curves 1) is determined by slightly ionized impurities, and is practically constant in the time interval under investigation. After the diffusion of the impurities (curve 2), the concentration of the current carriers is brought about by the ionization of the E_1 level which is partially compensated by the slightly ionized impurity ($0 < N_a < N$ for

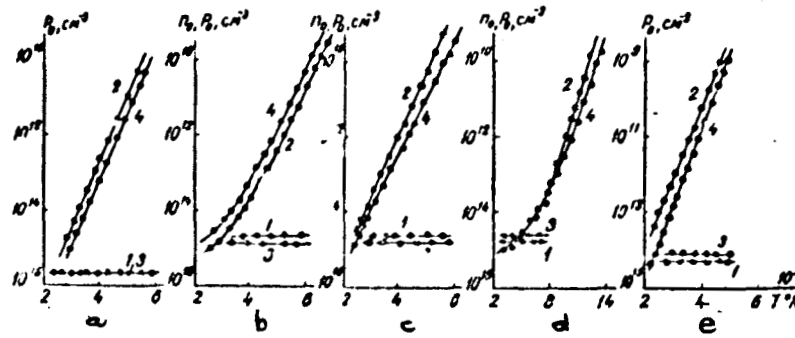


Figure 2. Temperature dependence of concentration of equiponderant current carriers in silicon on impurity atoms of Au (a), Zn (b), Pt (c), S (d) and Fe (e).

1, Original samples (a, d, e of p-type, and b, c of n-type; 2, after introduction of impurity (a, b, c, e of p-type, and d of n-type); 3, after deactivation of impurities (a, d, e of p-type, and b, c of n-type); 4, after activation of impurities (a, b, c, e of p-type, and d of n-type).

Au, Fe and S. and $0 < N_d < N$ for Zn and Pt),¹ hence, its exponential dependence on temperature (ref. 1). For Au and Fe impurities

$$p_0 = \frac{N_i}{N - N_i} Q_i e^{-\frac{E_i}{kT}} \ll N_i, \quad N - N_i;$$

for Pt and Zn impurities

$$p_0 = \frac{N - N_d}{N_d} Q_i e^{-\frac{E_i}{kT}} \ll N_d, \quad N - N_d;$$

¹

We should point out that during the introduction of Zn and Pt atoms into the p-type high-resistance samples we observed a similar temperature dependence p_0 . This is indicative of a partial compensation in them, E_{ta} , by the Zn and Pt interstitial atoms which, unlike the main atoms, are of a donor nature.

for S impurities

$$n_0 = \frac{N - N_s}{N_s} Q_0 e^{-\frac{E_s}{kT}} \ll N_s, \quad N - N_s$$

The annealing of such samples at 800°C (curves 3) resulted in a change /174 of the magnitude and temperature dependence of n_0 and p_0 . It appears that after such an annealing within this temperature range n_0 and p_0 are determined by slightly ionized impurities. A comparison of these samples with the initial ones (curves 1) shows that there is practically no difference between them.

Figure 3 (curves 2 and 3) contains typical data illustrating the change in the lifetime of $\tau_{\Phi n} \approx \tau_e + \tau_d$ and its temperature dependence measured by the modulation of the stationary photoconductivity itself (ref. 7) during the change of the Au impurity from an active to an inactive state. In the initial samples (curve 1) the lifetime is determined by residual impurities or defects of an unknown origin ($\tau_{\Phi n} \approx 100-20 \mu\text{sec}$), and its dependence on temperature is limited. After the introduction of the Au impurity into the p-type samples (curve 2) through the high-speed capture of unpaired electrons (δn) and holes (δp) partially compensated by the level E_{1d} ($U_{1e} = v S_{1e} N_a \delta n = v S_{1d} (N - N_a) \delta p = U_{1d}$) and level E_{2e} ($U_{2e} = v S_{2e} (N - N_a) \delta n = U_{2d}$) the life time $\tau_e = \delta n / U_{1e} + U_{2e}$ and $\tau_d = \delta p / U_{1d} + U_{2d}$ is sharply reduced ($\tau_{\Phi n} \approx 10^{-8}$ sec) and defined by the following correlation

$$\tau_e = \frac{1}{v S_{1e} N_a + v S_{2e} (N - N_a)}; \quad \tau_d = \frac{1}{v S_{1d} (N - N_a) \left(1 + \frac{v S_{2e} (N - N_a)}{v S_{1e} N_a} \right)}$$

where S_{1e} , S_{1d} and S_{2e} are the cross sections of the electron and hole capture by the appropriate level (ref. 7). Inasmuch as the level filling in the temperature range under investigation remains practically unchanged (fig. 2a), the $\tau_{\Phi n}$ temperature dependence is determined by a change in the capture cross

section. Annealing the samples at 800°C (curve 3) resulted in an increase of τ_{Φ_n} and change of its temperature dependence. But after the annealing, the lifetime is no longer determined by the impurities or defects but by the recombination, adhesion and capture centers which were originated by the high-temperature processing during the diffusion of the impurity, and were not eliminated by annealing at 800°C (ref. 5).

Similar data were obtained in the investigation of the recombination of the carriers with the Zn, Fe, Pt and S atoms in the samples.

A few words about the kinetics of inactivation. The inactivation rate varied with different impurities. Thus the concentration of Zn, Au and Pt atoms annealed at 800°C for 10-20 min was reduced by 60-90 percent, whereas the concentration of S changed by a similar percentage in two hours. The deactivation of impurities at low temperatures is considerably slower. Thus annealing at 600°C for two hours reduces the concentration of Zn, Au and Pt atoms by 60-90 percent. An abnormally high annealing rate was observed in the case of Fe atoms: they were deactivated by annealing at 200°C for 5-10 min.

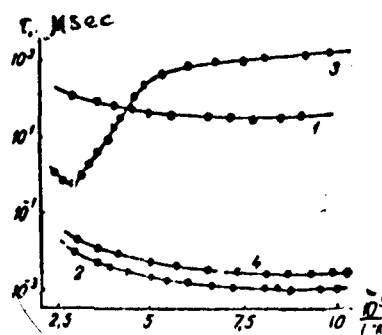


Figure 3. Temperature dependence of fixed lifetime of τ_{Φ_n} current carriers in p-type silicon. 1, Before introduction of Au impurities; 2, after introduction; 3, deactivation of the Au impurity; 4, activation.

It should be pointed out that, as in the case of Ge (ref. 8) and GaAs (refs. 9 and 10), the impurities deactivated in silicon leave a supersaturated solution of vacant positions each of which produces a slightly ionized acceptor level. The latter may considerably change the electron filling of the levels of the investigated impurities. This complicates the study of the kinetics of impurity deactivation following the n_e and p_0 change in the samples with a partially compensated impurity level.

In this way, the annealing of the samples with Au, Zn, Pt, Fe and S impurities at a temperature different from the temperature at which the impurities have been introduced changes them from an active state, in which they produce an effect on n_e , p_0 and $\tau_{\Phi n}$, into an inactive state, that is the impurities are deactivated. We should point out that this should be taken into account in the operations connected with the high-temperature treatment of silicon.

2. Activation of impurities. Cited in figure 2 (curves 4) are the 175 typical data illustrating the changing concentration and temperature dependence of the current carriers occasioned by the transition of the Au, Zn, Pt, Fe and S impurities from an inactive to an active state. Evidently, the result of the heating of the samples with deactivated Au, Zn, Pt, Fe and S impurities at temperatures equal to the diffusion temperature of the latter (1,200-1,250°C) was that the concentration of equivalent current carriers and their temperature dependence, just as after the diffusion of the investigated atoms, are determined by the ionization of the levels they have created (curves 4). A similar situation was observed also at different temperatures, higher than the impurity deactivation temperature.

Figure 3 (curve 4) illustrates the change in the lifetime of the current carriers $\tau_{\Phi n}$ produced by the transition of the Au impurity from an inactive to an active state when annealed at 1,200°C. Evidently the $\tau_{\Phi n}$ magnitude and temperature dependence are determined by the recombination on the Au atoms, just as immediately after the diffusion of the impurity. The thermal centers produced by the high-temperature treatment have practically no effect on the recombination of the current carriers, inasmuch as the recombination rate on them is considerably slower than on the impurity centers (refs. 7 and 11).

A similar situation was observed during the investigation of the carrier recombination on the Zn, Pt, Fe and S atoms.

Thus the annealing of the samples with deactivated impurities at temperatures different from the deactivation temperature is conducive to the transition of the impurities from an inactive state, in which they do not affect the n_e , p_0 and $\tau_{\Phi n}$, to an active state. We should point out that this should be taken into account in the high-temperature treatment of silicon.

3. A Discussion of the Results. These experiments show that the Au, Zn, Pt, Fe and S impurities can be changed from an active to an inactive state, and vice versa, by heat treatment at various temperatures. This can be explained by the fact that the solubility of the impurities in semiconductors depends on the temperature (fig. 4, ref. 2). The impurity with a C_1 solubility introduced into a semiconductor at temperature T_1 will remain in a metastable state at temperature T_2 which is different from T_1 , inasmuch as its C_2 solubility at this temperature will be replaced by the C_1 solubility of the investigated impurity found in the sample.

However, if the semiconductor is kept at temperature T_2 for an hour, a 176 new solubility of the impurity, equivalent to C_2 is established. If the

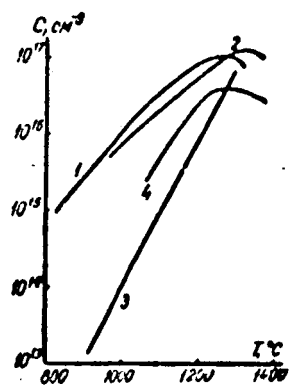


Figure 4. Temperature dependence of solubility impurities in silicon (refs. 2 and 3). 1, Au; 2, Zn; 3, Fe; 4, S.

solubility of the impurity at the annealing temperature is less than the one in the sample ($C_2 < C_1$), the surplus $C_1 - C_2$ spreads to the coagulation centers which might be volumetric structural defects (dislocations,¹ vacancies, the impurity atoms themselves and other atoms), as well as surface defects² (refs. 13 and 14). This process amounts to a deactivation of $C_1 - C_2$ impurity atoms at a given temperature. If the impurity solubility C_1 at annealing temperature is higher than the C_2 in the sample, and a surplus of knocked-on atoms is found in the coagulation centers, the $C_1 - C_2$ atoms are seen to spread from the coagulation centers to the lattice points and interstices.

¹The dislocation densities in this range (from a few to $2 \cdot 10^3 \text{ cm}^{-2}$ determined by the X-ray method (ref. 12)) were not the predominant coagulation centers in our experiments.

²The resulting effect of the coagulation centers on the surface is that the impurities of the subsurface layer are deactivated faster than inside. This should be taken into account when studying the kinetics of the deactivation processes.

The speed of the establishment of a new equivalent solubility (activation or deactivation) depends, of course, on the distance between the coagulation centers and the impurity diffusion factor at a given annealing temperature. The latter explains the dependence of the deactivation and activation rate on the temperature and the type of impurity which we have observed ($D_{800^{\circ}\text{C}} \gg D_{600^{\circ}\text{C}}$; $D_{\text{Fe}} \gg D_{\text{Au, Zn, Pt, S}}$ and $D_{\text{Au, Zn, Pt}} > D_{\text{S}}$ (refs. 2 and 3)).

We should point out that the concentration of the activated impurity may be somewhat smaller than the concentration of the impurity introduced at the same temperature by the diffusion method. This is due to the following. As we pointed out earlier, surface defects can also be impurity coagulation centers, as any type of heat treatment (including diffusion) brings some of the impurities to the surface. After the heat treatment, we ground off a 500μ thick layer from the surface. Part of the impurity coagulated on the surface was thus irretrievably lost, and the impurity concentration in the sample was reduced. Besides, the concentration of impurities was also reduced by evaporation in the course of high temperature treatment. That is why we observed an inadequate restoration of the electrical properties of the samples after their activation in a number of cases (figs. 2 and 3, curves 2 and 4).

In conclusion, we point out that the impurity deactivation phenomenon was studied in a number of semiconductors: Si (Fe (ref. 15), Ni (refs. 13, 16), Cu (refs. 14, 17), Co, Ag, Mn, Ur (ref. 17)); Ge (Li, Cu (refs. 8, 17), Ni (refs. 1, 8, 17), Fe, Co (ref. 1), Ag (ref. 18); GaAs (Li (ref. 10), Cu (ref. 9); CdS (Ag, Au, Cu (ref. 19)).

Inasmuch as the deactivation and activation phenomena are similar in nature, the presence of an activation process should be expected in the case of all impurities. Thus we observed the activation of a Cu impurity at 850°C in

germanium which had been deactivated beforehand at 450°C. We should point out that the observation of impurity activation in germanium is complicated by the fact that, unlike silicon, there is not much difference between the solubility of the investigated impurities and the thermal centers in them.

In conclusion, we will take this opportunity to express our gratitude to L. I. Datsenko for defining the dislocation density, and the research students V. O. Miroshnichenko of the Dnepropetrovsk State University and S. I. Khomenko of the Kiyev Engineering School for their assistance in the preparation and measurements of the samples.

Summary

The impurities in semiconductors may be found in an active and inactive state from the point of view of their effect on the electrophysical properties of the semiconductors (ref. 1). Annealing at 800°C changes the Au, Zn, Pt, Fe and S impurities from an active state, affecting the n_0 , p_0 and $\tau_{\Phi n}$, to an inactive state (figs. 2 and 3, curve 3), that is these impurities are deactivated. Annealing at 1,200°C the samples containing Au, Zn, Pt, Fe and S impurities in an inactive state changes them to an active state affecting the n_0 , p_0 and $\tau_{\Phi n}$ (figs. 2 and 3, curves 4), that is, these impurities are activated.

The observable patterns can be explained by the solubility-temperature dependence of the impurity in the semiconductors (ref. 2). The result of such a relationship is that the impurities found in the semiconductor at a temperature different from the temperature at which they were introduced may be in a metastable state, as their equiponderant solubility is different from the one in the sample (ref. 1). The establishment of a new state of equilibrium is connected with the existence of coagulation centers and the infusion of a

surplus of impurity atoms, if the equiponderant solubility is lower than the one in the sample (impurity deactivation), or with the diffusion of the impurity atoms from them into the lattice interstices, if the equiponderant solubility is higher than the one in the sample (impurity activation).

REFERENCES

1. Lashkarev, V. Ye., Miseluk, E. G. and Glinchuk, K. D. FTT, sb. statey, 1, 114, 1959.
2. Boltaks, B. I. Diffusion in Semiconductors (Diffuziya v poluprovodnikakh). Fizmatgiz, Moscow, 1961.
3. Carlson, A., Hall, R. and Peil, E. Phys. Chem. Solids, Vol. 8, 81, 1959.
4. Trousil, Z. Chekh. fiz. zh. Vol. 5, 393, 1955.
5. Glinchuk, K. D. and Litovchenko, N. M. FTT, Vol. 5, 3150, 1963;
Glinchuk, K. D., Denisova, A. D. and Litovchenko, N. M. Ukr. fiz. zh., Vol. 9, 805, 1964.
6. Woodbury, H. and Ludwig, G. Phys. Rev., Vol. 126, 466, 1962.
7. Glinchuk, K. D., Denisova, A. D. and Litovchenko, N. M. FTT, Vol. 5, 1933, 1963; Glinchuk, K. D. and Litovchenko, N. M. FTT, Vol. 5, 3003, 1963.
8. Henney, N. B. Semiconductors (Poluprovodniki). Moscow, I. L., Ch. 6, 1962.
9. Whelan, J. and Fuller, C. J. Appl. Phys., Vol. 31, 1507, 1960.
10. Light, T. and Wolfstirn, K. J. Appl. Phys., Vol. 35, 1649, 1964.
11. Glinchuk, K. D. and Litovchenko, N. M. Ukr. fizichi zh., Vol. 8, 575, 1963.
12. Datsenko, L. I. FTT, Vol. 4, 524, 1962.

13. Yoshida, M. J. Phys. Soc. Japan, Vol. 17, 1677, 1962.
14. Thomas, W. Solid State Physics (Phisica status solidy). Vol. 3, 2261,
1963; Vol. 7, 685, 1964.
15. Shepard, W. and Turner, J. Phys. Chem. Solids, Vol. 23, 1697, 1962.
16. Shattes, W. and Wegener, H. J. Appl. Phys., Vol. 29, 866, 1958.
17. Blilough (sic), B. and Newman, R. Progress in Semiconductors. Vol. 7,
122-134, London, 1963.
18. Glinchuk, K. D., Miseluk, Ye. G. and Fortunatova, N. N. FTT, Vol. 1,
1345, 1959.
19. Dreeben, A. J. Electrochem. Soc., 111, 174, 1964.

Institute of Semiconductors,
Ukrainian Academy of Sciences,
Kiev

Submitted to the
editor 13 June 1964.